Vibrational energy transfer across a reverse micelle surfactant layer

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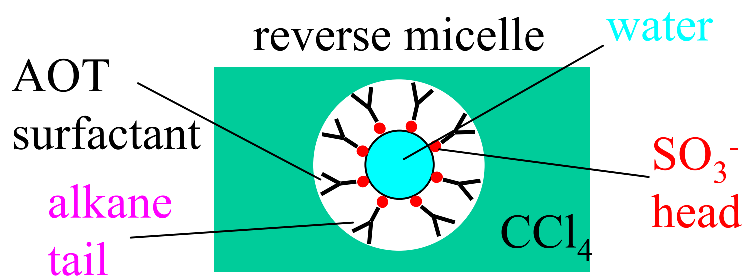
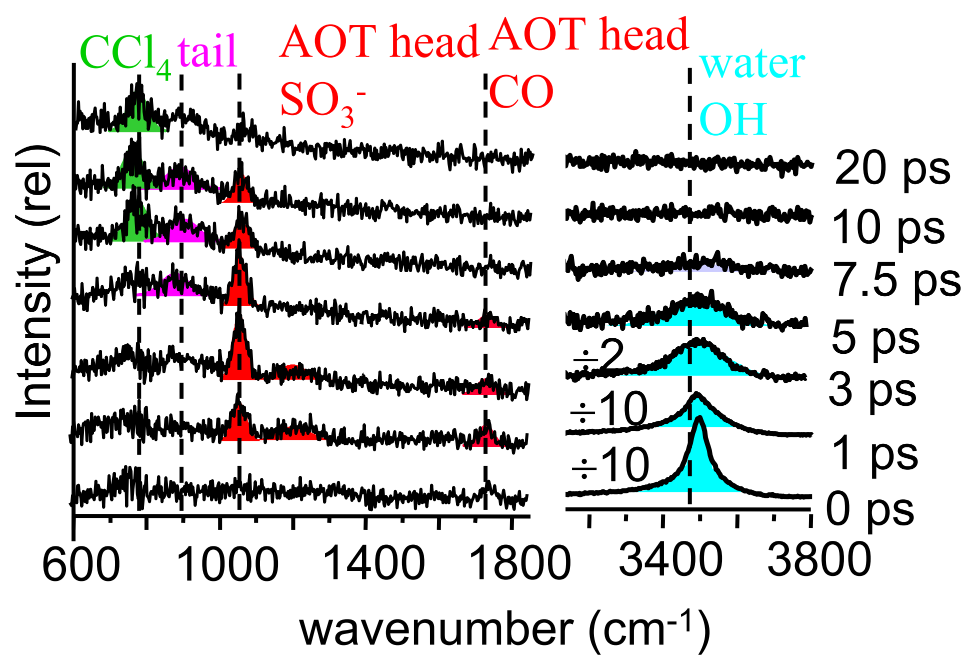
The flow of vibrational energy across a molecular monolayer separating water from CCl_4 was measured using vibrational spectroscopy. In reverse micelles consisting of ~35 water molecules surrounded by a monolayer of AOT surfactant, a femtosecond IR pulse excited water vibrations. A Raman probe pulse monitored the flow of vibrational energy within 10 picoseconds, from water to the AOT sulfate head group and AOT CO, through the AOT alkane tail and out to the CCl_4.

The results were quite different than would be expected for ordinary heat transfer. The shape of the molecules really matters for heat flow across a single molecule layer.





Moving upward in time, vibrational energy in the water moves to the AOT head, then to the AOT tail and finally to CCl_4 in about 10 picoseconds.

Who?, Where?, What?, and So What?.

This work was a collaborative effort between the University of Illinois and the University of Scranton. Prof. John Deak and undergraduate Tim Sechler fabricated the reverse micelle suspensions, characterized them by vibrational spectroscopy and brought them to Illinois. Postdoc Zhahoui Wang and graduate student Yoonsoo Pang from Dana Dlott's lab did the femtosecond spectroscopy experiments at Illinois.

This group showed it was possible to watch vibrational energy flow through a molecular monolayer that separates an aqueous phase and a nonpolar solvent phase. Reverse micelles were used, that consisted of about 35 water molecules, a coating of about 18 AOT surfactant molecules, forming a spherical assembly about 35Å in diameter, suspended in CCl_4 solvent. A femtosecond infrared pump, Raman probe method has been developed in the Dlott lab with support from NSF DMR. A series of Raman spectra were obtained when either the OH stretch of water or CH stretch of the AOT were excited by a femtosecond infrared pulse. The Raman spectra show the vibrational energy as it leaves the water, flows through the AOT polar head groups, through the AOT tail and out to the CCl_4 in about 10 ps. When the AOT tails were pumped, vibrational energy took much longer, about 40 ps, to reach the CCl_4. This is exactly the opposite of what would occur in ordinary thermal conduction. One has to look at the precise pathways for molecular vibrational energy transfer to understand how this occurs. The efficiency by which the water energy is channeled outside suggests strategies to design molecular nanosystems that can efficiently conduct away vibrational energy, which is needed for high speed operation of future molecular nanomachines.

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This work was a collaborative effort between the University of Illinois and the University of Scranton. The researchers who contributed to this project were Prof. Dana D. Dlott, Graduate Student Yoonsoo Pang and Post-doctoral Fellow Zhaohui Wang from Illinois, and Prof. John Deàk and Undergraduate Tim Sechler from Scranton.

Broader Impacts

Vibrational energy is released in almost every chemical transformation. We have demonstrated the ability to watch the flow of vibrational energy through molecular nanostructures in real time, which will greatly aid our understanding of nanomaterial transformations.

As technology progresses toward making electronic and mechanical devices from individual molecules, the ability to run at high speeds requires efficient heat dissipation. We have now shown that vibrational energy flow through a layer one molecule thick into bulk phases is not a traditional heat conduction problem, instead requiring an analysis of the detailed pathways for vibrational energy. This work helps explain how to design molecules that transport and dissipate vibrational energy with high efficiency.